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FABRIC TREATMENTTechnical Field

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The present invention relates to garment treatment compositions suitable for domestic use in a laundering process, and in particular to compositions which contain components which can cross-link with cellulose.

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Background of the Invention

Cellulose is a beta 1-4 linked polysaccharide and the principal component of cotton, which is a well-known material for the production of fabrics and in very widespread use. Cellulose is capable of cross-linking by hydrogen bonds which form between the cellulose chains.

20 The majority of garments purchased world-wide contain at least some cellulose fibres in the form of cotton or rayon and these suffer from the well-known problem that on exposure to water, such as during domestic laundering, fibre dimensions change and cause shrinking, shape change and  
25 wrinkling of the garments. It is believed that this is due to release and reformation of hydrogen bonds.

So-called 'durable press' treatments of fabrics are intended to overcome these difficulties. One of the most common  
30 methods of durable pressing uses a crosslinking agent to immobilise cellulose at a molecular level. Known cross-

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linking agents for whole cloth include formaldehyde, and urea-glyoxal resins. Other proposals include epichlorohydrins, vinyl sulphones, acrylo-amide and acrylo-acrylates. None of these proposed technologies have  
5 demonstrated any commercial viability for domestic on finished garments use to date.

A range of industrial processes for use in the manufacture of finished fabrics are known.

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US 4588761 discloses poly-urethane coating compositions for use with a transfer paper or other temporary support. These comprise an isocyanate which is preferably blocked. This is an industrial treatment process for fabric and is inherently  
15 unsuitable for use at home on finished garments.

JP 53035098 discloses a finishing process for treating woven or knitted cellulosic fabrics with a processing solution comprising a urethane prepolymer with blocked terminal  
20 isocyanate groups, a gloxal-amide type cross-linking agent and a bromo-fluorinated metal. The process is not suitable for domestic application to finished garments.

JP6346374 discloses finishing of fabric or a sewed product  
25 by a stepwise industrial process comprising treatment with a blocked isocyanate, heat treatment and subsequent use of a gas phase cross-linking agent. A similar process is disclosed in JP8127972.

30 JP 55093882 discloses a method for flocked fabric production which uses masked isocyanate. JP 9316781 discloses a

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finishing agent for use in the production of yarn, paper or films which comprises a blocked isocyanate. JP 11131374 discloses an industrial process for the product of water repellent fabric by treatment with a glyoxal-based resin crosslinking agent, an organo-fluorine compound and a isocyanate based cross-linking agent. Followed by heat treatment for 0.5-5min. A similar process is disclosed in JP 2000129573.

10 An alternative proposal is to use poly-acids such as BTCA (butyl tetra carboxylic acid) or citric acid as crosslinking agents. These can esterify with the -OH groups of the cellulose to form a covalent cross-link. The covalent cross-link is not disrupted by water and this both prevents deformation of fabrics and assists return to a flat state. One of the difficulties with this approach is that a sodium hypophosphite catalyst is generally used to cause the esterification reaction to proceed and the treated articles require heat curing. Moreover, these poly-acid materials are highly water soluble and are difficult to deposit on fabrics.

A preferred durable press system suitable for domestic use should be a non-toxic, one component, catalyst-free system with low iron-cure times, have some affinity for the fabric surface and not cause fabric strength losses. It should also avoid the need for specialised equipment and the use of use of difficult materials such as vapour-phase formaldehyde.

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**Brief Description of the Invention**

We have determined that excellent cross-linking benefits can be obtained by treating finished garments with a cellulose cross-linking agent that is thermally activated.

Accordingly, the present invention provides a method of treating finished garments comprising cellulosic material so as to cause cross-linking, which comprises the step of treating fabrics with an effective amount of a blocked cross-linking agent for cellulose, said cross-linking agent being thermally activated.

In the context of the present invention, the term 'thermally activated' is intended to mean that the cross-linking agent is 'blocked' to prevent reaction until the cross-linking agent is activated by the application of heat. In order to achieve cross-linking is preferable that at least two reactive sites of the cross-linking agents are blocked with a thermally labile blocking group.

Preferably the blocked cross-linking sites are selected such that, when activated, they are readily capable of reacting with hydroxy groups present in cellulose. More preferably the cross-linking reaction forms an 'ester' linkage, which in the context of the present invention includes linkages where the alpha carbon of the ester is replaced by a hetero-atom, preferably nitrogen. In the case of the alpha-carbon being so replaced the molecule is formally known as a carbamate.

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Ideally, the reaction proceeds without the requirement for a catalyst. Catalysts can optionally be present. Suitable catalysts are selected depending on the particular blocking chemistry employed and, for example, include, pH  
5 modification agents and/or metal ions.

Preferably the cross-linking agent is bi-functional.

In one preferred embodiment of the invention the cross-  
10 linking agent is an at least bi-functional blocked polycarboxylic acid.

In another preferred embodiment of the invention the cross linking agent is an at least bi-functional blocked  
15 isocyanate.

By 'bi-functional' is meant that there are at least two blocked groups which can act as cross linking sites. Preferably, both of these are either blocked isocyanates or  
20 blocked carboxylic acids.

Preferably the blocked carboxylic acid is an ester with relatively weak ester bonds which can trans-esterify with cellulose. This is accomplished by forming the polyester  
25 between a poly-carboxylic acid and an alcohol (which term includes phenol) which is a good leaving group. The alcohols act as thermally labile 'blocking agents' for the carboxylic acid groups. Essentially the same result can be obtained by the use of carboxylic acid/imide linkages.

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The present invention provides a method of treating finished garments comprising cellulosic materials so as to cause cross-linking which comprises the step of transesterifying the cellulosic material with an effective amount of an at  
5 least bi-functional blocked polycarboxylic acid.

Preferably said blocked polycarboxylic acid is blocked with an electron-withdrawing alcohol or imide.

10 The present invention further provides a method of treating finished garments comprising cellulosic materials so as to cause cross-linking which comprises the step of treating finished garments comprising cellulosic material with an effective amount of an at least bi-functional blocked  
15 isocyanate.

In the present invention the treatment is conducted as part of a domestic laundering operation applied to finished garments.

20

A further aspect of the present invention provides a composition for use in the methods described above.

Preferably, said composition will comprise a cross-linking  
25 agent which forms an ester linkage with the cellulose.

Preferably the cross-linking agent comprises either a blocked poly isocyanate or blocked poly carboxylic acid and which is thermally activated.

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Preferably, the method of the invention comprises the step of curing the treated materials by heat treatment at a temperature of from 50 to 250C, more preferably at a temperature of from 100-200C.

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More preferably, the method of the present invention further comprises the step of curing the treated materials by ironing or hot pressing. That a useful effect can be obtained by ironing after treatment is surprising.

10

Advantageously, the present method may be performed in the absence of vapour-phase formaldehyde and other components known from the prior art which are unsuitable for domestic use.

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#### Detailed Description of the Invention

As noted above the cellulose cross-linking agent can be a polycarboxylic acid or a blocked isocyanate. Preferred  
embodiments of each of these alternatives are discussed in further detail below.

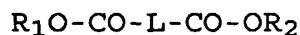
In some embodiments the backbone of the cross-linking agent is polymeric in character, by which is meant that it comprises repeating structures. Typically, the backbone comprises a sufficiently long polymeric structure (preferably 2-12 carbon-carbon bond lengths) to fulfil its function as a bridging structure between the two or more  
reactive groups.

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**A. Blocked Polycarboxylicacids:**

Polyesters suitable for use in the present invention comprise a polycarboxylic acid esterified with a 'leaving' group which is an alcohol or an imide. The polycarboxylic acid preferably has 2-6 carboxyl groups available for esterification. Typically each of the carboxyl groups will be esterified to produce a polyester.

Most preferably, the polycarboxylic acid has two carbonyl groups available for esterification and typically these are at opposite ends of an essentially linear polycarboxylic acid. In a preferred embodiment the polyester takes the form:



Where  $R_1O-$  and  $-OR_2$  are the same or different alcohol residues, and  $-CO-L-CO-$  is the residue of the polycarboxylic acid. L is a linking group, which may be substituted, and generally comprises a 2-12 carbon backbone.

**Polycarboxylic acids:**

Preferred polycarboxylic acids include one or more of :  
malonic Acid, methylmalonic acid, ethylmalonic acid, butylmalonic acid, dimethylmalonic acid, diethylmalonic acid;



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succinic acid, methylsuccinic acid, 2,2-dimethylsuccinic acid, 2-ethyl-2-methylsuccinic acid, 2,3-dimethylsuccinic acid, meso-2,3-dimethylsuccinic acid, glutaric acid,

5 2-methylglutaric acid, 3-methylglutaric acid, 2,2-dimethylglutaric acid, 3,3-dimethyl-glutaric acid, adipic acid, 3-methyladipic acid, 3-tert-butyladipic acid,

pimelic acid,

10 suberic acid,

azelic acid,

sebacic acid,

1,11-undecanecarboxylic acid, undecanedioic acid, 1,10-decanedicarboxylic acid,

15 1,12-dodecanedicarboxylic acid,

hexadecanedioic acid,

docosanedioic acid,

tetracosanedioic acid,

tricarballic acid,

20 1,2,3,4-butanetetracarboxylic acid,

itaconic acid,

maleic acid,

fumaric acid,

citraconic acid,

25 mesaconic acid,

trans-glutaconic acid,

trans-beta-hydromuconic acid,

trans-traumatic acid,

trans,trans-muconic acid,

30 cis-aconitic acid, trans-aconitic acid,

malic acid, citramalic acid,

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isopropylmalic acid,  
3-hydroxy-3-methylglutaric acid,  
tartaric acid,  
mucic acid,  
5 citric acid,  
dihydroxyfumaric acid,  
diglycolic acid,  
3,6-dioxaoctanedioic acid,  
3,3'-thiodipropionic acid, 3,3'-dithiodipropionic acid,  
10 trans-DL-1,2-cyclopentanedicarboxylic acid,  
3,3-tetramethyleneglutaric acid,  
camphoric acid,  
cyclohexylsuccinic acid,  
1,1-cyclohexanediacetic acid,  
15 trans-1,2-cyclohexanedicarboxylic acid,  
1,3-cyclohexanedicarboxylic acid, 1,4-  
cyclohexanedicarboxylic acid,  
1,3,5-cyclohexanetricarboxylic acid,  
Kemp's triacid,  
20 1,2,3,4-cyclobutanetetracarboxylic acid,  
1,2,3,4,5,6-cyclohexanehexacarboxylic acid  
4-Carboxyphenoxyacetic acid,  
1,4-phenylenediacetic acid,  
1,4-phenylenedipropionic acid,  
25 1,4-phenylenediacrylic acid,  
2-Carboxybenzenepropanoic acid,  
4,4'-oxybis(benzoic acid),  
phthalic acid, isophthalic acid, terephthalic acid,  
1,2,3-benzenetricarboxylic acid, 1,3,5-  
30 benzenetricarboxylic acid,  
1,2,4,5-benzenetetracarboxylic acid,

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mellitic acid,  
2-methoxyisophthalic acid,  
diphenic acid,  
4,4'-biphenyldicarboxylic acid,  
5 2,6-Napthalenedicarboxylic acid,  
3-carboxy-1,4-dimethyl-2-pyrroleacetic acid,

Oligomers (and co-oligomers) of unsaturated carboxylic acids  
can be used. Suitable materials include oligomers of  
10 acrylic acid, methacrylic acid, crotonic acid, vinylacetic  
acid, 4-pentenoic acid, and/or maleic acid

The acid can comprise a heteroatom. Nitrogen is a preferred  
heteroatom. Suitable N-containing acids include:

15 iminodiacetic acid,  
3-aminophthalic acid, 2-aminoterephthalic acid, 5-  
aminoisophthalic acid,  
ethylenediamine-N,N'-diacetic acid,  
methylinimodiacetic acid,  
20 nitrilotriacetic acid,  
ethylenediaminetetraacetic acid,  
1,6-diaminohexane-N,N,N',N'-tetraacetic acid,  
trans-1,2-diaminocyclohexane-N,N,N',N',-tetraacetic  
acid,  
25 triethylenetetraminehexaacetic acid,  
1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic  
acid,  
ethylenebis(oxyethylenenitrilo)tetraacetic acid,  
diethylenetriaminepentaacetic acid,  
30 aspartic acid,  
glutamic acid,

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2-methylglutamic acid,  
2-aminoadipic acid,  
3-aminoadipic acid,  
2,6-diaminopimelic acid,  
5 cystine  
N-benzyliminodiacetic acid,  
N-(2-carboxyphenyl)glycine,  
2,2'-(ethylenedioxy)dianiline-N,N,N',N'-tetraacetic  
acid.  
10 porphobilinogen,  
4,5-imidazoledicarboxylic acid,  
2,2'-bipyridine-4,4'-dicarboxylic acid,  
3,4-pyridinedicarboxylic acid, 2,5-  
pyridinedicarboxylic acid, 3,5-pyridinedicarboxylic acid,  
15 2,6-pyridinedicarboxylic acid,  
6-methyl-2,3-pyridinedicarboxylic acid,  
2,6-dimethyl-3,5-pyridinedicarboxylic acid

In the case where a nitrogen is present, this may be  
20 quaternerised with an appropriate quaternerising agent.  
Known quaternerising agents include  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{I}$ , and  
 $(\text{CH}_3)_2\text{SO}_4$ .

#### Alcohols:

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The alcohol may have a linear, branched or ring structure.

Preferred alcohols comprise 5- or 6-membered rings which  
have electron-withdrawing groups in the ortho- and para-  
30 positions relative to the alcoholic hydrogen. Examples of

- 13 -

such preferred alcohols include N-hydroxysuccinimide and hydroxybenzotriazole. In addition, the alcohol may be in the enol form of a ketone. As noted above, and for the avoidance of doubt, phenols are considered alcohols for the purpose of this specification.

Suitable electron withdrawing substituents on the ring include one or more of : NO<sub>2</sub>, CN, CO<sub>2</sub>H, CO<sub>2</sub>R, CONHR, CONR<sub>2</sub>, CHO, COR, SO<sub>2</sub>R, SO<sub>2</sub>OR, SO<sub>2</sub>OAr, NO, Ar, NR<sub>3</sub><sup>⊕</sup>, SR<sub>2</sub><sup>⊕</sup>, NH<sub>3</sub><sup>⊕</sup>, F, Cl, Br, I, OAr, SH, SR, OH, OR, CH=CR<sub>2</sub>. The electron withdrawal can be due to either inductive or resonance effects.

Phenol derivatives with at least one electron-withdrawing substituent are preferred.

Preferred phenol derivatives include:

Vanillin,  
Ethyl vanillin,  
Eugenol,  
isoeugenol,  
salicylic acid, ethyl salicylate,  
4-cyanophenol,  
hydroxyacetophenone,  
trichlorophenol,  
2,6-dimethoxyphenol,  
4-aminophenol (and quaternerised salt),  
dimethylaminophenol (and quaternerised salt),  
chlorophenol, bromophenol, iodophenol, fluorophenol,  
dichlorophenol, dibromophenol, diiodophenol, difluorophenol,

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hydroxythiophenol,  
aminocresol,  
4-amino-2,5-dimethylphenol,  
6-amino-2,4-dichloro-3-methylphenol,  
5 nitrophenol, dinitrophenol,  
hydroxypropiophenone,  
2'-hydroxy-5'-methylacetophenone,  
5'-chloro-2'-hydroxyacetophenone,  
acetovanillone,  
10 4-hydroxybenzaldehyde,  
o-vanillin,  
4-hydroxy-3-methylbenzaldehyde,  
2-chloro-4-hydroxybenzaldehyde,  
2-hydroxy-5-methoxybenzaldehyde,  
15 3-ethoxy-4-hydroxybenzaldehyde,  
5-nitrovanillin,  
3-methoxy-5-nitrosalicylaldehyde,  
4-hydroxybenzoic acid,  
methylsalicylic acid,  
20 chlorosalicylic acid,  
methoxysalicylic acid,  
aminosalicylic acid,  
methylsalicylic acid,  
formylsalicylic acid,  
25 hydroxyisophthalic acid,  
methyl hydroxybenzoate,  
ethyl hydroxybenzoate,  
propyl hydroxybenzoate,  
methyl 5-methylsalicylate,  
30 ethyl 5-methylsalicylate,  
hydroxybenzamide,

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5-chloro-2-hydroxybenzamide,  
5-acetylsalicylamide,  
2-amino-4-(ethylsulfonyl)phenol

- 5 Particularly preferred alcohols include trichlorophenol, isoeugenol, vanillin, 4-cyanophenol, ethyl salicylate, 2,6-dimethoxy phenol, 4-aminophenol and dimethylamino phenol. As noted above, imides can also be used as the 'alcohol'.
- 10 A preferred imide material is N-hydroxysuccinimide.

The alcohol leaving group can have functional properties which give it some utility after the transesterification reaction. One such property is that of a perceptible odour.

15 For example, a notable odour of cloves is obtained with weak isoeugenol esters upon the application of heat (i.e. on ironing). This can act as a useful cue to the user that the reaction is proceeding.

- 20 Preferred polyesters include the trichlorophenol diester of succinic acid, the trichlorophenol diester of BTCA, the N-hydroxysuccinimide diester of succinic acid, the isoeugenol diester of succinic acid, and the vanillin diester of succinic acid.

25 The polyester will typically only have one type of alcohol present, although it is possible to envisage 'mixed' esters in which two or more, different types of alcohol are present.

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It is particularly preferred that the polyester has a molecular weight below 1500 Dalton. It is believed that the cellulosic materials will stiffen if larger molecular weight materials are used.

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While the polyester can be applied from a non-aqueous solvent (such as THF) it is preferable to apply the material from a wholly or partly aqueous solvent.

10 **B. Blocked Polyisocyanates:**

In another class of embodiments of the invention the treatment agent is a blocked isocyanate.

15 Blocked isocyanate is described at length and defined in 'Progress in Organic Coatings' 36 (1999) 148-172.

Preferably, but not exclusively, the blocked isocyanate is chemically blocked. Such molecules include materials which  
20 are derived from isocyanate compounds by reaction with an active hydrogen compound. However, it is also known to produce blocked isocyanate via other routes not involving the reaction of an isocyanate, these are still known in the art as blocked isocyanate. Similarly, while cross-linking  
25 most reactions of the blocked isocyanate will generate an isocyanate as an intermediate, reaction schemes have been suggested in which the blocked isocyanate reacts without the formation of such an intermediate. It is also known that isocyanate can form thermally unstable dimers or higher  
30 polymeric forms, generally known as 'uretdiones' these are



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also considered to be examples of blocked isocyanate for the purposes of the present invention.

As suitable polycarboxylic acids and 'blocking' alcohols  
5 were described above, so suitable polyisocyanates and blocking groups are described below.

**Polyisocyanates:**

- 10 1,4-Diisocyanatobutane
- 1,6-Diisocyanatohexane
- 1,8-Diisocyanatooctane
- 1,10-Diisocyanatodecane
- 1,12-Diisocyanatododecane
- 15 Tetradecamethylenediisocyanate
- Trimethylhexanediisocyanate
- Tetramethylhexanediisocyanate
- trans-1,4-cyclohexylene diisocyanate
- Isophorone diisocyanate
- 20 1,3-Bis(isocyanatomethyl)cyclohexane
- 4,4'-methylenebis(cyclohexyl isocyanate)
- Trimethylolpropane triisocyanate
- 1-isocyanato-2,4-bis[(4-isocyanatocyclohexyl)methyl]-  
cyclohexane
- 25  $\alpha$ ,4-Tolylene diisocyanate
- m-xylene diisocyanate
- Toluene 2,4-diisocyanate
- Toluene 2,5-diisocyanate
- 1,3-Bis(1-isocyanato-1-methylethyl)benzene
- 30 1,3-Phenylene diisocyanate
- 1,4-Phenylene diisocyanate

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2,6-Tolylene diisocyanate  
4,4'-oxybis(phenyl isocyanate)  
Naphthylene-1,5-diisocyanate  
Triphenyl methane-4,4',4''-triisocyanate  
5 2,4-diisocyanato-1-(4-isocyanatophenoxy)-benzene  
1,3,5-triisocyanato-2-methyl-benzene  
Diphenylmethane-2,4,4'-triisocyanate

Also envisaged as suitable are biuret-isocyanurate- or  
10 urethane-group-containing modification products of the above  
mentioned simple polyisocyanates, for example tris-(6-  
isocyanatohexyl)-biuret and its higher homologs;  
polyisocyanates containing isocyanurate groups obtainable by  
the trimerisation of aliphatic and/or aromatic diisocyanates  
15 such as hexamethylene diisocyanate, isophorone diisocyanate,  
especially tri-(6-isocyanatohexyl)-isocyanurate

Polyisocyanates formed by the reaction of an excess of  
diisocyanate with polyhydric alcohols followed by the  
20 removal of unreacted diisocyanate excess by distillation.

Examples of simple polyhydric alcohols include:

Glycerol  
25 1,2-dihydroxypropane  
Trimethylol propane  
Pentaerythritol  
Ethyleneglycol  
Diethyleneglycol  
30 Triethyleneglycol  
Tetraethyleneglycol

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Pentaethyleneglycol

Hexaethylene glycol

Polyethyleneglycol

Polypropyleneglycol

5 Dipentaerythritol

Triethanolamine (which can be optionally quaternerised)

The diisocyanates can also be reacted with polyols containing anionic groups such as carboxylic acids, sulphone  
10 acids and phosphoric acids, and especially hydroxyacids followed by removal of excess unreacted diisocyanate by distillation in a similar manner. Suitable hydroxyacids include:

15 2,2-bis(hydroxymethyl)acetic acid  
2,2-bis(hydroxymethyl)propionic acid  
2,2-bis(hydroxymethyl)butionic acid  
2,2,2-tris(hydroxymethyl)acetic acid  
Tartaric acid

20

The acid groups can optionally be partially or completely neutralised to make the isocyanate-containing molecule water soluble or water dispersible.

25 Polyisocyanates can also be formed by reaction of diisocyanates with polyamines followed by removal of excess unreacted diisocyanate by distillation.

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- 20 -

Examples of suitable polyamines include:

Diethylenetriamine

N-(2-aminoethyl)-1,3-propanediamine

5 3,3'-diamino-N-methyldipropylamine

N-(3-aminopropyl)-1,3-propanediamine

Spermidine

Bis(hexamethylene)triamine

2,2'-(ethylenedioxy)bis(ethylamine)

10 4,7,10-trioxa-1,13-tridecanediamine

Glycerol tris(poly(propylene glycol)amine terminated)

ether

Chitosan

15 Polyisocyanates formed by the conversion from polyamines,  
for example by treatment with phosgene are also included.

Hexamethylene diisocyanate is a particularly preferred isocyanate  
for use in the present invention.

20

#### **Polyisocyanate Blocking Agents:**

These are analogous to the thermally-labile alcohol blocking  
agents used for the esters and described above. As in the  
25 case of the preferred materials described for blocking  
esters the blocking agents for the isocyanates can also be  
phenols. As noted above the isocyanates generally react with  
cellulose to form carbamates, which are considered examples  
of the more general class of esters. It is believed that  
30 some isocyanates, will however react to form 'true' esters.

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Preferred phenols again have electron withdrawing substituents in the ortho and/or para position relative to the alcoholic proton.

- 5 Oximes, (an oxime is formed by the reaction of hydroxylamine with a carbonyl compound) can be used to block isocyanates. Examples of suitable ketones that form oximes by reaction with hydroxylamine include:

- 10 Tetramethylcyclobutanedione  
Methyl n-amyl ketone  
Methyl isoamyl ketone  
Methyl 3-ethylheptyl ketone  
Methyl 2,4-dimethylpentyl ketone  
15 Methyl ethyl ketone  
Cyclohexanone  
Methyl isopropyl ketone  
Methyl isopropyl ketone  
Methyl isobutyl ketone  
20 Diisobutyl ketone  
Methyl t-butyl ketone  
Diisopropyl ketone  
2,2,6,6-Tetramethylcyclohexanone

- 25 Suitable non-phenol alcohol blocking agents include:

Mono-ethers of ethylene glycol such as 2-ethoxyethyl alcohol, 2-ethoxyethoxyethyl alcohol, 2-ethylhexyloxyethyl alcohol, 2-butoxyethyl alcohol, and 2-butoxyethoxyethyl  
30 alcohol

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N,N-Glycol amides such as N,N-dibutylglycolamide  
N-hydroxysuccinimide

Suitable amides and imides blocking agents include:

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Acetanilide  
N-methylacetamide  
Caprolactam  
2-pyrrolidone  
Succinimide

10

Suitable imidazole and amidine blocking agents include:

2-ethyl-4-methylimidazole  
2-methylimidazole  
1,4,5,6-tetrahydropyrimidine  
guanidine  
2,4-dimethylimidazoline  
4-methylimidazoline  
2-phenylimidazoline  
4-methyl-2-phenylimidazoline

15

20

Suitable Pyrazole and triazole blocking agents include:

pyrazole  
3-methylpyrazole  
3,5-dimethylpyrazole  
1,2,4-triazole  
Benzotriazole

25

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Secondary and especially hindered amines can be used to block isocyanates.

Suitable active methylene blocking agents include:

5

diethyl malonate

t-butyl methyl malonate

Meldrum's acid (isopropylidene malonate)

Ethyl acetoacetate

10

t-butyl acetoacetate

Particularly preferred blocking agents are Meldrum's Acid, Phenol, 4-Nitrophenol, 4-Methoxyphenol, and/or Methyl Salicylate. The most preferred blocking agents are diethyl malonate, succinimide and sodium bisulphite.

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Both the isocyanates and the carboxylic acids described above can be mono-blocked by reaction of only one of the characteristic reactive groups by a suitable blocking agent. The remaining free reactive group(s) can then be reacted with a bi-functional further linking group (such as a polyol or polyamine) to form blocked structures which (taking the mono-blocked acids and a diol as an example) have the form:



Where:

30  $R_1O-$  and  $-OR_2$  are the same or different alcohol residues,

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-CO-L1-CO- and -CO-L2-CO- are the same or different residue of polycarboxylic acid, and, -OMO- is the residue of the polyol.

5 Similar structures can be prepared from the isocyanates.

Methods of forming mono-blocked isocyanates include blocking of diisocyanates where each isocyanate group has a different reactivity thus one or more groups become preferentially  
10 blocked. Alternatively, the blocking agent can be added to a large excess of diisocyanate and the unreacted diisocyanate removed by distillation upon completion of blocking. Similar considerations apply to esters.

15 Reaction of the mono-blocked cross-linking agent with either a polyol or polyamine can involve either reaction with all the available hydroxy or amine groups to give a 100% modified polyol or polyamine.

20 By controlling the amount of mono-blocked cross-linking added, structures with both modified and unmodified hydroxy and amine groups can be formed. Such structures are capable of self-crosslinking upon removal of the blocking groups.

25 Suitable polyols include those found among the alcohols described previously as being suitable for blocking isocyanates or carboxylic acids.



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Particularly preferred polyols are:

Sugars such as sorbitol, mannitol, xylose, fructose, galactose, mannose, glucose, altrose, lactose, cellobiose, sucrose,

5       Oligo and polysaccharides, preferentially  $\beta$ -1,4-linked oligo- and polysaccharides.

Particularly preferred are polyols are cellulose and its derivatives, or other polysaccharides which have the ability  
10 to recognise cellulose, example of which include locus bean gum and guar gum.

Suitable polyamines include:

Diethylenetriamine  
15       N-(2-aminoethyl)-1,3-propanediamine  
      3,3'-diamino-N-methyldipropylamine  
      N-(3-aminopropyl)-1,3-propanediamine  
      Spermidine  
      Bis(hexamethylene)triamine  
20       2,2'-(ethylenedioxy)bis(ethylamine)  
      4,7,10-trioxa-1,13-tridecanediamine  
      Glycerol tris(poly(propylene glycol)amine terminated)  
ether  
      Chitosan

25       Optionally, unreacted amino groups can be rendered cationic by modification with quaternerising agents such as methyl iodide, dimethyl sulphate and the like. Such cationic modification improves the substantivity of the materials.

30

- 26 -

By use of a secondary linking group 'M' which can recognise (as in the case of polysaccharides) or otherwise bind (as in the case of the cationics) to a cellulosic substrate the efficiency of deposition of the cross-linking agents can be significantly improved.

#### **Carriers and Product Form:**

Compositions of the present invention are preferably formulated into fabric care compositions comprising a solution, dispersion or emulsion comprising a cross-linking agent.

The compositions of the invention will generally comprise a textile compatible carrier.

In the context of the present invention the term "textile compatible carrier" includes a component which can assist in the interaction of the cellulose cross-linking agent with a textile. The carrier can be a simply a solvent for the cross-linking agent, although the carrier can also provide benefits in addition to those provided by the cross-linking agent e.g. softening, cleaning etc. Preferably, the carrier is a detergent-active compound or a textile softener or conditioning compound or a detergent.

If the composition is to be used in a laundry process as part of a conventional fabric treatment product, such as a rinse conditioner or main wash product, it is preferable if the level of cross-linking agent is from 0.01% to 10%, more

- 27 -

preferably 0.05% to 7.5%, most preferably 0.1 to 5wt% of the total composition.

If, however, the composition is to be used in a laundry process as a product to specifically treat the fabric to reduce creasing, higher levels of cross-linking agent can be used. Preferred amounts are from 0.01% to 15%, more preferably 0.05% to 10%, for example from 0.1 to 7.5wt% of the total composition.

If the composition is to be used in a spray product it is preferred that the level of cross-linking agent is from 0.5 to 20 wt%, preferably 1 to 20 wt% of the total composition.

As noted above, the method of the invention generally comprises the step of applying a composition of the cross-linking agent to garments and curing the composition, preferably by ironing. The composition may be applied to the fabric by conventional methods such as dipping, spraying or soaking, for example.

The fabric care composition of the invention preferably comprises a solution, dispersion or emulsion comprising a cross-linking agent and a textile compatible carrier. The textile compatible carrier facilitates contact between the fabric and the ingredients of the composition. The textile compatible carrier may be water or a surfactant. However, when it is water, it is preferred that a perfume is present.

In one particularly preferred embodiment, the composition may be provided in a form suitable for spraying onto a

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fabric. The fabric may then be dried, e.g. in a tumble dryer, and then ironed to cure the composition.

If this is the case, it is preferred that the polycarboxylic acid or derivative thereof is present at a level from 0.5 to 20wt%, preferably 0.5 to 10wt%, of the total composition. If the product is to be used in a spray on product it is also beneficial if wetting agents are also present such as alcohol ethoxylates for example, Synperonic A7.

For a spray on formulation anionic surfactants may be present.

Suitable spray dispensing devices are disclosed in WO 96/15310 (Procter & Gamble) and are incorporated herein by reference. Alternatively, the composition may be applied through the irons water tank, a separate reservoir or a spray cartridge in an iron, as described in EP1201816 and WO 99/27176.

Spray products may contain water and/or other solvents as a carrier molecule.

It is particularly advantageous, and surprising, that the composition can be cured by ironing, even under domestic conditions. Moreover, a steam iron can be used, which is desirable to aid wrinkle removal, with no deleterious effects on the curing process.

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A further advantage of the method of the invention is that, when the composition is applied as a spray, one application is sufficient to obtain benefits after subsequent washes.

5 In a washing process, as part of a conventional textile washing product, such as a detergent composition, the textile-compatible carrier will typically be a detergent-active compound. Whereas, if the textile treatment product is a rinse conditioner, the textile-compatible carrier will  
10 be a textile softening and/or conditioning compound. These are described in further detail below.

The cross-linking agent can be used to treat the textile in the wash cycle of a laundering process. The cross-linking  
15 agent can also be used in the rinse cycle, or, preferably applied prior to or during ironing and/or pressing.

The composition of the invention may be in the form of a liquid, solid (e.g. powder or tablet), a gel or paste,  
20 spray, stick or a foam or mousse. Examples include a soaking product, a rinse treatment (e.g. conditioner or finisher) or a main-wash product. Spray products are particularly suited to application as part of an ironing or pressing process.

25 Liquid compositions may also include an agent which produces a pearlescent appearance, e.g. an organic pearlising compound such as ethylene glycol distearate, or inorganic pearlising pigments such as microfine mica or titanium  
30 dioxide (TiO<sub>2</sub>) coated mica. Liquid compositions may be in the form of emulsions or emulsion precursors thereof.

- 30 -

**Detergent Active Compounds:**

If the composition of the present invention is itself in the  
5 form of a detergent composition, the textile-compatible  
carrier may be chosen from soap and non-soap anionic,  
cationic, nonionic, amphoteric and zwitterionic detergent  
active compounds, and mixtures thereof.

10 Many suitable detergent active compounds are available and  
are fully described in the literature, for example, in  
"Surface-Active Agents and Detergents", Volumes I and II, by  
Schwartz, Perry and Berch.

15 The preferred textile-compatible carriers that can be used  
are soaps and synthetic non-soap anionic and nonionic  
compounds.

Anionic surfactants are well-known to those skilled in the  
20 art. Examples include alkylbenzene sulphonates,  
particularly linear alkylbenzene sulphonates having an alkyl  
chain length of C<sub>8</sub>-C<sub>15</sub>; primary and secondary alkylsulphates,  
particularly C<sub>8</sub>-C<sub>15</sub> primary alkyl sulphates; alkyl ether  
sulphates; olefin sulphonates; alkyl xylene sulphonates;  
25 dialkyl sulphosuccinates; and fatty acid ester sulphonates.  
Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary  
and secondary alcohol ethoxylates, especially the C<sub>8</sub>-C<sub>20</sub>  
30 aliphatic alcohols ethoxylated with an average of from 1 to

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20 moles of ethylene oxide per mole of alcohol, and more especially the C<sub>10</sub>-C<sub>15</sub> primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated  
5 nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

Cationic surfactants that may be used include quaternary ammonium salts of the general formula  $R_1R_2R_3R_4N^+ X^-$  wherein  
10 the R groups are independently hydrocarbyl chains of C<sub>1</sub>-C<sub>22</sub> length, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising cation (for example, compounds in which R<sub>1</sub> is a C<sub>8</sub>-C<sub>22</sub> alkyl group, preferably a C<sub>8</sub>-C<sub>10</sub> or C<sub>12</sub>-C<sub>14</sub> alkyl group, R<sub>2</sub> is a methyl group, and R<sub>3</sub>  
15 and R<sub>4</sub>, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters) and pyridinium salts.

The total quantity of detergent surfactant in the  
20 composition is suitably from 0.1 to 60 wt% e.g. 0.5-55 wt%, such as 5-50wt%.

Preferably, the quantity of anionic surfactant (when present) is in the range of from 1 to 50% by weight of the  
25 total composition. More preferably, the quantity of anionic surfactant is in the range of from 3 to 35% by weight, e.g. 5 to 30% by weight.

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Preferably, the quantity of nonionic surfactant when present is in the range of from 2 to 25% by weight, more preferably from 5 to 20% by weight.

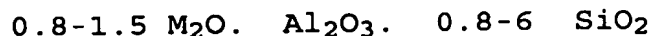
- 5 Amphoteric surfactants may also be used, for example amine oxides or betaines.

**Builders:**

- 10 The compositions may suitably contain from 10 to 70%, preferably from 15 to 70% by weight, of detergency builder. Preferably, the quantity of builder is in the range of from 15 to 50% by weight.

- 15 The detergent composition may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate.

- The aluminosilicate may generally be incorporated in amounts  
20 of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50%. Aluminosilicates are materials having the general formula:



25

where M is a monovalent cation, preferably sodium. These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g.

- The preferred sodium aluminosilicates contain 1.5-3.5 SiO<sub>2</sub>  
30 units in the formula above. They can be prepared readily by



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reaction between sodium silicate and sodium aluminate, as  
amply described in the literature.

Alternatively, or additionally to the aluminosilicate  
5 builders, phosphate builders may be used.

**Textile Softening and/or Conditioner Compounds:**

If the composition of the present invention is in the form  
10 of a textile conditioner composition, the textile-compatible  
carrier will be a textile softening and/or conditioning  
compound (hereinafter referred to as "textile softening  
compound"), which may be a cationic or nonionic compound.

15 The softening and/or conditioning compounds may be water  
insoluble quaternary ammonium compounds. The compounds may  
be present in amounts of up to 8% by weight (based on the  
total amount of the composition) in which case the  
compositions are considered dilute, or at levels from 8% to  
20 about 50% by weight, in which case the compositions are  
considered concentrates.

Compositions suitable for delivery during the rinse cycle  
may also be delivered to the textile in the tumble dryer if  
25 used in a suitable form. Thus, another product form is a  
composition (for example, a paste) suitable for coating  
onto, and delivery from, a substrate e.g. a flexible sheet  
or sponge or a suitable dispenser during a tumble dryer  
cycle.

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Suitable cationic textile softening compounds are substantially water-insoluble quaternary ammonium materials comprising a single alkyl or alkenyl long chain having an average chain length greater than or equal to C<sub>20</sub>. More preferably, softening compounds comprise a polar head group and two alkyl or alkenyl chains having an average chain length greater than or equal to C<sub>14</sub>. Preferably the textile softening compounds have two, long-chain, alkyl or alkenyl chains each having an average chain length greater than or equal to C<sub>16</sub>.

Most preferably at least 50% of the long chain alkyl or alkenyl groups have a chain length of C<sub>18</sub> or above. It is preferred if the long chain alkyl or alkenyl groups of the textile softening compound are predominantly linear.

Quaternary ammonium compounds having two long-chain aliphatic groups, for example, distearyldimethyl ammonium chloride and di(hardened tallow alkyl) dimethyl ammonium chloride, are widely used in commercially available rinse conditioner compositions. Other examples of these cationic compounds are to be found in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch. Any of the conventional types of such compounds may be used in the compositions of the present invention.

The textile softening compounds are preferably compounds that provide excellent softening, and are characterised by a chain melting L $\beta$  to L $\alpha$  transition temperature greater than

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25°C, preferably greater than 35°C, most preferably greater than 45°C. This L $\beta$  to L $\alpha$  transition can be measured by DSC as defined in "Handbook of Lipid Bilayers", D Marsh, CRC Press, Boca Raton, Florida, 1990 (pages 137 and 337).

5

Substantially water-insoluble textile softening compounds are defined as textile softening compounds having a solubility of less than  $1 \times 10^{-3}$  wt % in demineralised water at 20°C. Preferably the textile softening compounds have a  
10 solubility of less than  $1 \times 10^{-4}$  wt%, more preferably less than  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  wt%.

Especially preferred are cationic textile softening compounds that are water-insoluble quaternary ammonium  
15 materials having two C<sub>12-22</sub> alkyl or alkenyl groups connected to the molecule via at least one ester link, preferably two ester links. Di(tallowoxyloxyethyl) dimethyl ammonium chloride and/or its hardened tallow analogue are especially preferred of the compounds of this type. Other preferred  
20 materials include 1,2-bis(hardened tallowoxyloxy)-3-trimethylammonium propane chloride. Their methods of preparation are, for example, described in US 4 137 180 (Lever Brothers Co). Preferably these materials comprise small amounts of the corresponding monoester as described in  
25 US 4 137 180, for example, 1-hardened tallowoxyloxy-2-hydroxy-3-trimethylammonium propane chloride.

Other useful cationic softening agents are alkyl pyridinium salts and substituted imidazoline species. Also useful are

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primary, secondary and tertiary amines and the condensation products of fatty acids with alkylpolyamines.

The compositions may alternatively or additionally contain  
5 water-soluble cationic textile softeners, as described in  
GB 2 039 556B (Unilever).

The compositions may comprise a cationic textile softening  
compound and an oil, for example as disclosed in  
10 EP-A-0829531.

The compositions may alternatively or additionally contain  
nonionic textile softening agents such as lanolin and  
derivatives thereof.

15 Lecithins are also suitable softening compounds.

Nonionic softeners include L $\beta$  phase forming sugar esters (as  
described in M Hato et al Langmuir 12, 1659, 1666, (1996))  
20 and related materials such as glycerol monostearate or  
sorbitan esters. Often these materials are used in  
conjunction with cationic materials to assist deposition  
(see, for example, GB 2 202 244). Silicones are used in a  
similar way as a co-softener with a cationic softener in  
25 rinse treatments (see, for example, GB 1 549 180).

The compositions may also suitably contain a nonionic  
stabilising agent. Suitable nonionic stabilising agents are  
linear C<sub>8</sub> to C<sub>22</sub> alcohols alkoxylated with 10 to 20 moles of  
30 alkylene oxide, C<sub>10</sub> to C<sub>20</sub> alcohols, or mixtures thereof.

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Advantageously the nonionic stabilising agent is a linear C<sub>8</sub> to C<sub>22</sub> alcohol alkoxyated with 10 to 20 moles of alkylene oxide. Preferably, the level of nonionic stabiliser is within the range from 0.1 to 10% by weight, more preferably from 0.5 to 5% by weight, most preferably from 1 to 4% by weight. The mole ratio of the quaternary ammonium compound and/or other cationic softening agent to the nonionic stabilising agent is suitably within the range from 40:1 to about 1:1, preferably within the range from 18:1 to about 3:1.

The composition can also contain fatty acids, for example C<sub>8</sub> to C<sub>24</sub> alkyl or alkenyl monocarboxylic acids or polymers thereof. Preferably saturated fatty acids are used, in particular, hardened tallow C<sub>16</sub> to C<sub>18</sub> fatty acids.

Preferably the fatty acid is non-saponified, more preferably the fatty acid is free, for example oleic acid, lauric acid or tallow fatty acid. The level of fatty acid material is preferably more than 0.1% by weight, more preferably more than 0.2% by weight. Concentrated compositions may comprise from 0.5 to 20% by weight of fatty acid, more preferably 1% to 10% by weight. The weight ratio of quaternary ammonium material or other cationic softening agent to fatty acid material is preferably from 10:1 to 1:10.

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**Other Components**

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Compositions according to the invention may comprise soil release polymers such as block copolymers of polyethylene oxide and terephthalate.

10 Other optional ingredients include emulsifiers, electrolytes (for example, sodium chloride or calcium chloride) preferably in the range from 0.01 to 5% by weight, pH buffering agents, and perfumes (preferably from 0.1 to 5% by weight).

15

Further optional ingredients include non-aqueous solvents,, fluorescers, colourants, hydrotropes, antifoaming agents, enzymes, optical brightening agents, and opacifiers.

20 Suitable bleaches include peroxygen bleaches. Inorganic peroxygen bleaching agents, such as perborates and percarbonates are preferably combined with bleach activators. Where inorganic peroxygen bleaching agents are present the nonanoyloxybenzene sulphonate (NOBS) and tetra-  
25 acetyl ethylene diamine (TAED) activators are typical and preferred.

Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

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In addition, compositions may comprise one or more of anti-shrinking agents, anti-wrinkle agents, anti-spotting agents, germicides, fungicides, anti-oxidants, UV absorbers (sunscreens), heavy metal sequestrants, chlorine scavengers, dye fixatives, anti-corrosion agents, drape imparting agents, antistatic agents and ironing aids. The lists of optional components are not intended to be exhaustive.

In order that the invention may be further and better understood it will be described below with reference to several non-limiting examples.

### Examples

#### Synthesis Examples:

Example 1: Synthesis of 2,4,6-Trichlorophenol Diester of Butanetetracarboxylic Acid

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Butane tetracarboxylic acid (BTCA) (20.84g, 0.089mol) and 2,4,6-trichlorophenol (35.80g, 0.18mol) were weighed into a RB flask (250cm<sup>3</sup>). Nitrogen was flushed through the flask for 15 minutes, then distilled THF (150cm<sup>3</sup>) was added. After stirring under nitrogen for 30 minutes, diisopropylcarbodiimide (29.0cm<sup>3</sup>, 0.18mol) was added dropwise over 20 minutes. The reaction was allowed to stir overnight under nitrogen. The mixture was filtered, washed with THF then stirred for one hour to ensure that formation of precipitate

- 40 -

was complete. The solvent was removed to afford the crude product. This was washed several times with dichloromethane to yield the product upon removal of the solvent from the filtrate.

5

**Example 2:        Synthesis of 2,4,5-Trichlorophenol Diester of Succinic Acid**

---

10

Succinic acid (1.5g, 0.013mol) was dissolved in DMSO (50cm<sup>3</sup>). 1,1'-Carbonyldiimidazole (5.0g, 0.03mol) was added and the mixture stirred for 30mins at room temperature. 2,4,5-Trichlorophenol (5.05g, 0.026mol) was then added and the mixture stirred at room temperature overnight. The mixture was added to water, filtered, then washed with water followed by diethyl ether to yield a white solid (2.03g, 33%)  $\delta_H$  (500 MHz; CDCl<sub>3</sub>) 3.07 (4H, s, CH<sub>2</sub>-CH<sub>2</sub>-C(O)-O-) and 7.55 & 7.29 (4H, s, Ph).

20

**Example 3:        Synthesis of N-Hydroxysuccinimide Diester of Succinic Acid**

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25

Succinic acid (2.0g, 0.017mol) was dissolved in THF (50cm<sup>3</sup>). 1,1'-Carbonyldiimidazole (5.49g, 0.034mol) was added and the mixture stirred for 30mins at room temperature. N-Hydroxysuccinimide (3.89g, 0.034mol) was added and the mixture stirred at room temperature overnight. The mixture

30



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was added to water, filtered, then washed with water then diethyl ether to yield a white solid (2.0g, 38%)

$\delta_H$  (500 MHz;  $CDCl_3$ ) 2.59 (8H, s,  $CH_2-CH_2-CO-N-$ ) and 2.89 (4H, s,  $CH_2-CH_2-C(O)-O-$ )

5

**Example 4:        Synthesis of Vanillin Diester of Succinic Acid**

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10

*(1) Organic solvent method:*

Vanillin (9.82 g, 64.5 mMols) was dissolved in anhydrous THF ( $100\text{ cm}^3$ ) with stirring at room temperature and under

15 nitrogen. Anhydrous sodium carbonate (8.2 g, 77.4 mMols, 1.2 equiv) was then added and stirring was continued for 30 mins. Succinyl chloride (5 g, 32.25 mMols, 0.5 equiv) was then added dropwise to the slurry over 20 mins, the mixture was then stirred in the dark for a further 18 hours. The  
20 mixture was then filtered and the solvent removed from the filtrate under reduced pressure to give an off-white solid. The crude product was then recrystallised from IPA to give a white solid (2.7 g, 24 %).  $\delta_H$  (500 MHz;  $CDCl_3$ ) 3.08 (2H, s,  $-CH_2-C(O)-O-$ ), 3.89 (3H, s,  $-OCH_3$ ), 7.27 - 7.50 (3H, m, Ph)  
25 and 9.95 (1H, s,  $-CHO$ ).

*(2) Schotten-Baumann method:*

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Sodium Hydroxide (1.3 g, 32.5 mmols) was dissolved in distilled water (100 cm<sup>3</sup>). To this solution vanillin (4.91 g, 32.5 mmols) was added and the solution was stirred to give a light yellow solution. The solution was then cooled to 0 °C prior to the dropwise addition of succinyl chloride (2.5 g, 16.25 mmols). The mixture was then allowed to warm to room temperature and stirring was continued for a further 10 mins to give a light yellow precipitate. The mixture was then poured into water (200 cm<sup>3</sup>) and stirred at room temperature for 30 mins. The solution was filtered and the solid material retained. This crude product was then recrystallised to give a white solid (0.84 g, 13 %).

**Example 5:        Synthesis of 4-Cyanophenol Diester of Succinic Acid**

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4-Cyanophenol (7.7 g, 64.5 mMols) was dissolved in anhydrous THF (100 cm<sup>3</sup>) with stirring at room temperature and under nitrogen. Anhydrous sodium carbonate (8.2 g, 77.4 mMols, 1.2 equivalents) was then added and stirring was continued for a further 10 mins. Succinyl chloride was then added dropwise over 20 mins and the mixture was stirred under nitrogen for a further 18 hours in the dark. The grey slurry was filtered and the solvent was removed from the filtrate under reduced pressure to give a grey solid. This crude material was then recrystallised from IPA to give a off-white solid (3.7 g, 36 %).  $\delta_H$  (500 MHz; CDCl<sub>3</sub>) 3.03 (2H,

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s,  $-\text{CH}_2-\text{C}(\text{O})-\text{O}-$ ), 7.24 (2 H, d, J 8, Ph). & 7.69 (2 H, d, J 8.5, Ph).

5 **Example 6:        Synthesis of Isoeuginol Diester of Succinic Acid**

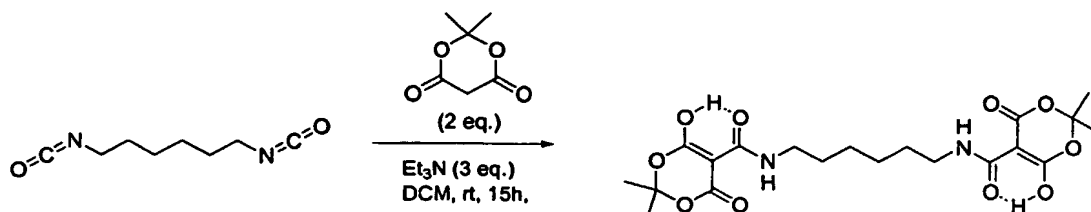
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Isoeuginaol (25g, 0.15mol) was dissolved in THF ( $100\text{cm}^3$ ).  
10 Sodium carbonate (16.14g, 0.15mol) was added and the mixture stirred at room temperature. Succinyl chloride (11.8g, 0.075mol) was added to the stirred mixture over 20 minutes, and the mixture stirred for a further 90 minutes. The reaction mixture was then heated to  $50^\circ\text{C}$  for 60 mins, then  
15 stirred at room temperature overnight. The mixture was filtered and the solvent removed under reduced pressure to give a dark coloured oil which solidified upon standing. This crude material was recrystallised from ethyl acetate and diethyl ether to give an off-white solid (4.67g, 8%)  $\delta_{\text{H}}$   
20 (500 MHz;  $\text{CDCl}_3$ ) 1.86 (6H, d,  $-\text{CH}_3-\text{CH}=\text{CH}-$ ), 3.80 (6H, s, Ph  $\text{CH}_3$ ), 6.34 - 6.14 (4H, m,  $\text{CH}=\text{CHCH}_3$ ) and 6.70-6.88 (6H, m, Ph).

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**Example 7: Synthesis of Hexamethylene diisocyanate blocked with Meldrum's Acid.**

5 **Synthesis:**



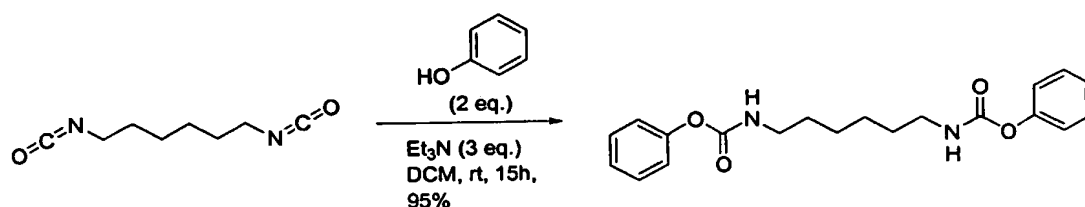
At room temperature a mixture of diisocyanatohexane (5.0 mL, 30.92 mmol, 1 eq.) and Meldrum's acid (9.36 g, 64.92 mmol, 2.1 eq.) in dichloromethane (100 mL) was treated with triethylamine (12.9 mL, 92.75 mmol, 3.0 eq.) in a dropwise fashion. Stirring was continued for 15 hours. TLC analysis (EtOAc) indicated no remaining Meldrum's acid. Silica (ca. 25 g) was added and the solvent was removed *in vacuo*.

15 Purification by flash column chromatography afforded the diamide (7.33 g, 55%) as a colourless solid.  $R_f = 0.1$  (EtOAc);  $\delta_H$  (400 MHz,  $CDCl_3$ ) 1.42-1.46 (4H, m,  $CH_2$ ), 1.59-1.68 (4H, m,  $CH_2$ ), 1.69-1.74 (12H, s(br),  $CH_3$ ), 3.42 (4H, q,  $J$  6.5 Hz,  $CH_2$ ), 9.25-9.34 (2H, s(br), NH), 14.95-15.0 (2H, s(br), OH);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 26.2 ( $CH_2$ ), 26.2 ( $CH_3$ ), 28.9, 40.3 ( $CH_2$ ), 72.8 (C-quaternary), 104.6, 164.2 (C=), 170.25, 170.3 (CO);  $m/z$  ( $ES^+$ ) 477 ( $M-H^++2Na^+$ , 100%); Found C, 51.49; H, 6.05; N, 5.98;  $C_{18}H_{28}N_2O_{10}$  requires C, 50.00; H, 6.48; N, 6.48.

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**Example 8: Synthesis of Hexamethylene diisocyanate blocked with Phenol**

Synthesis:

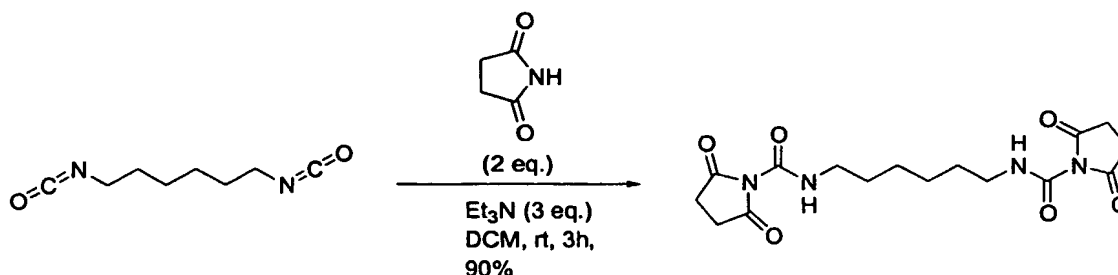


- Diisocyanatohexane (1.0 mL, 6.18 mmol, 1 eq.) and phenol (1.26 g, 13.39 mmol, 2.1 eq.) in dichloromethane (25 mL) was treated with triethylamine (2.7 mL, 19.37 mmol, 3.1 eq.) in a dropwise fashion. Stirring was continued for 15 hours. The solvent was removed under reduced pressure and the solid obtained was dried in a vacuum desiccator. Thus, the title compound (2.16 g, 98%) was obtained as a white solid.  $\delta_H$  (400 MHz,  $CDCl_3$ ) 1.36-1.44 (4H, m,  $CH_2$ ), 1.54-1.65 (4H, m,  $CH_2$ ), 3.26 (4H, q(br),  $J$  6.5 Hz,  $CH_2$ ), 5.05 (2H, m(br), NH), 7.12 (4H, d,  $J$  7.5 Hz, ArH), 7.18 (2H, t,  $J$  7.5 Hz, ArH), 7.34 (4H, t,  $J$  7.5 Hz, ArH);  $\delta_C$  (100 MHz,  $CDCl_3$ ) 26.2, 29.7, 41.0 ( $CH_2$ ), 121.6 (CH), 125.2 (C-ipso), 129.2 (CH), 151.1 (C-ipso), 154.6 (CO); Found C, 66.00; H, 7.02; N, 8.27;  $C_{20}H_{24}N_2O_4$  requires C, 67.42; H, 6.74; N, 7.87.

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**Example 9: Synthesis of Hexamethylene diisocyanate blocked with Succinimide**

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**5 Synthesis:**

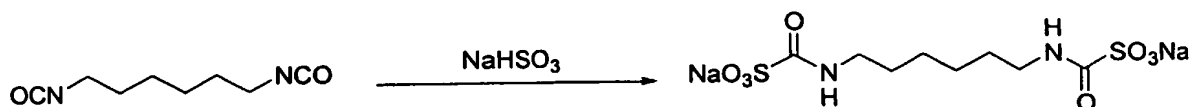
At room temperature a solution of diisocyanatohexane (7.57 g, 45.01 mmol, 1 eq.) and succinimide (8.90 g, 90.01 mmol, 2.0 eq.) in dichloromethane (100 mL) was treated with triethylamine (18.8 mL, 135.0 mmol, 3.0 eq.) in a dropwise fashion. Stirring was continued for 1 hour. The white precipitate formed was collected by filtration and washed with dichloromethane (3 x 50 mL) and dried in a vacuum desiccator. Thus, the title compound (14.93 g, 90%) was obtained as a white (colourless) powder.  $\delta_H$  (270 MHz, d<sub>6</sub>-DMSO) 1.12-1.45 (8H, m, CH<sub>2</sub>), 2.64 (8H, s, CH<sub>2</sub>), 3.01 (4H, q, *J* 6.5 Hz, CH<sub>2</sub>), 9.25-9.34 (2H, t, *J* 6.5 Hz, NH); Found C, 52.28; H, 6.04; N, 15.30; C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub> requires C, 52.46; H, 6.01; N, 15.30.

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**Example 10: Synthesis of Hexamethylene diisocyanate blocked with Sodium Bisulphite**

5

Synthesis:



10 In a 100mL round-bottom flask containing a magnetic stirrer bar, hexamethylene diisocyanate (6.73g, 0.04M) was added sodium metabisulphite (8.36g, 0.044M) dissolved in 16 mL of water and the turbid solution covered and stirred for 17 hours at room temperature (20°C). The product was precipitated in acetone (100mL) filtered and dried. The product was dissolved in water (30mL) then precipitated with  
15 acetone (350mL), filtered and dried in vacuo, resulting in a fine white powder in 93% yield\*.

20 FTIR confirmed the formation of CONH (1680 cm<sup>-1</sup>) and lack of an isocyanate peak (2275 cm<sup>-1</sup>) indicated that no free diisocyanate was present.

\*NMR assay (internal trioxan standard) confirmed a purity of 57.43% . The impurities probably are sodium metabisulphite.

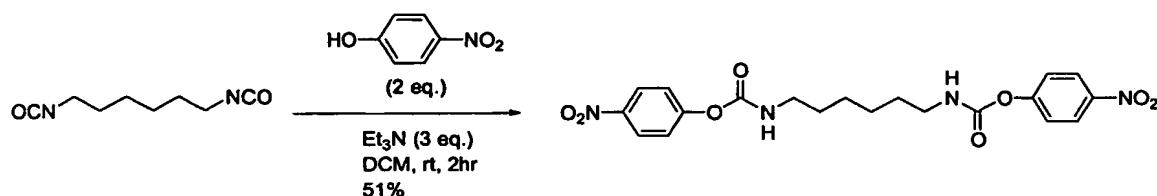
25 <sup>1</sup>H NMR - (D<sub>2</sub>O): δ (ppm) 1.36 (4H, m); 1.55 (water, s); 1.59 (4H, m); 2.23 (acetone, s); 3.29 (4H, t); 4.74 (D<sub>2</sub>O); 5.23 (trioxan, 6H, s).

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**Example 11: Synthesis of Hexamethylene diisocyanate blocked with 4-Nitrophenol**

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5    **Synthesis:**



Diisocyanatohexane (4.1 mL, 25.35 mmol, 1 eq.) and 4-nitrophenol (7.06 g, 50.75 mmol, 2.0 eq.) in dichloromethane (100 mL) was treated with triethylamine (7.1 mL, 50.75 mmol, 2.0 eq.) in a dropwise fashion. Stirring was continued for 2 hours. The yellowish precipitate formed was collected by filtration and washed with dichloromethane (2 x 50 mL), Et<sub>2</sub>O (1 x 50 mL) and dried in a vacuum desiccator. Thus, the title compound (11.25 g, 100%) was obtained as a white-yellow powder.  $\delta_{\text{H}}$  (400 MHz, d<sub>6</sub>-DMSO) 1.31-1.45 (4H, m, CH<sub>2</sub>), 1.46-1.59 (4H, m, CH<sub>2</sub>), 3.10 (4H, t(br), *J* 6.5 Hz, CH<sub>2</sub>), 7.40 (4H, d, *J* 9.0 Hz, ArH), (2H, t(br), *J* 6.5 Hz, NH), 8.28 (4H, d, *J* 9.0 Hz, ArH); Found C, 52.28; H, 6.04; N, 15.30; C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>O<sub>6</sub> requires C, 52.46; H, 6.01; N, 15.30.

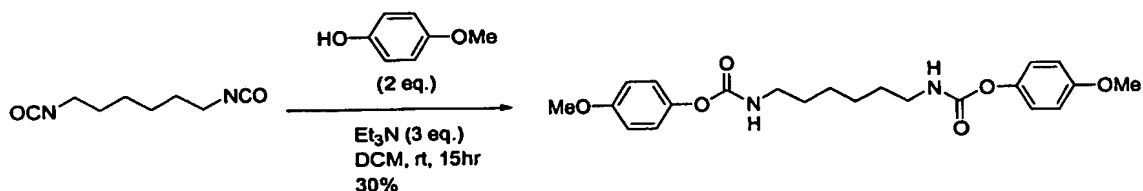


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**Example 12: Synthesis of Hexamethylene diisocyanate blocked with 4-Methoxyphenol**

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**5 Synthesis:**

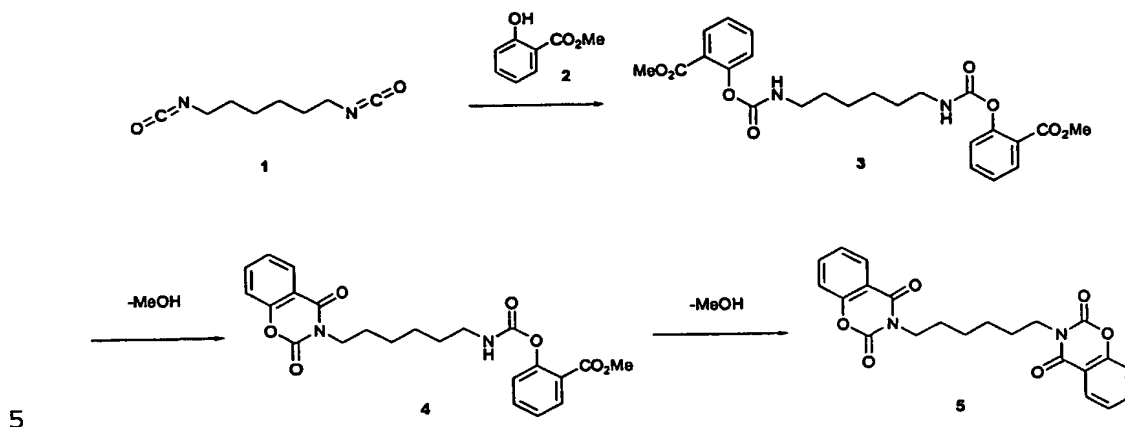


Diisocyanatohexane (3.5 mL, 21.58 mmol, 1 eq.) and 4-methoxyphenol (5.36 g, 43.17 mmol, 2.0 eq.) in  
 10 dichloromethane (50 mL) was treated with triethylamine (9.0 mL, 64.76 mmol, 3.0 eq.) in a dropwise fashion. Stirring was continued for 15 hours. The white precipitate formed was collected by filtration and washed with dichloromethane (2 x 50 mL) and dried in a vacuum desiccator. Thus, the  
 15 title compound (5.0 g, 59%) was obtained as a white powder.  
 $\delta_H$  (400 MHz, d<sub>6</sub>-DMSO) 1.25-1.42 (4H, m, CH<sub>2</sub>), 1.45-1.55 (4H, m, CH<sub>2</sub>), 3.07 (4H, q(br), *J* 6.0 Hz, CH<sub>2</sub>), 3.36 (6H, s, CH<sub>3</sub>), 6.90 (4H, d, *J* 9.0 Hz, ArH), 7.02 (4H, d, *J* 9.0 Hz, ArH), 7.61 (2H, t(br), *J* 6.0 Hz, NH);  $\delta_C$  (100 MHz, d<sub>6</sub>-DMSO) 26.3, 29.5, 40.7 (CH<sub>2</sub>), 55.7 (CH<sub>3</sub>), 114.5, 122.9 (CH), 144.9, 155.1 (C-ipso), 156.6 (CO); Found C, 62.58; H, 7.08; N, 7.66; C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub> requires C, 61.22; H, 7.14; N, 7.14.

20

- 50 -

**Example 13: Synthesis of Hexamethylene diisocyanate blocked with Methyl Salicylate**



Diisocyanatohexane 1 (0.9 mL, 5.57 mmol, 1 eq.) and the phenol 2 (1.50 g, 10.38 mmol, 1.9 eq.) in dichloromethane (50 mL) was treated with triethylamine (2.3 mL, 16.69 mmol, 3.0 eq.) in a dropwise fashion. Stirring was continued for 15 hours. The solvent was removed under reduced pressure and the crude reaction mixture was purified by flash column chromatography (Hex-EtOAc; 2:1 → 1:1) affording the title compound (4) as a white (colourless) crystalline solid (0.725 g, 29%) was obtained as a white powder.  $R_f = 0.15$  (Hex-EtOAc; 1:1);  $m/z$  ( $ES^+$ ) 463 ( $MNa^+$ , 100%);  $\delta_H$  (250 MHz,  $CDCl_3$ ) 1.32-1.95 (8H, m,  $CH_2$ ), 3.23 (2H, q,  $J$  6.5 Hz,  $CH_2$ ), 3.82 (3H, s,  $CH_3$ ), 4.02 (2H, t,  $J$  7.0 Hz,  $CH_2$ ), 5.29 (1H, m(br), NH), 7.12 (1H, d,  $J$  7.5 Hz, ArH), 7.20-7.34 (3H, m, ArH), 7.51 (1H, dt,  $J$  1.5, 7.5 Hz, ArH), 7.69 (1H, dt,  $J$  1.5, 7.5 Hz, ArH), 7.96 (1H, dd,  $J$  1.5, 7.5 Hz, ArH), 8.08

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(1H, dd,  $J$  1.5, 7.5 Hz, ArH); found C, 61.9; H, 5.5; N, 6.2%,  $C_{23}H_{24}O_7N_2$  requires C, 62.7; H, 5.45; N, 6.4%.

#### Application Examples:

5 In the examples 14-19 and 27 given below, the synthesised esters were pad applied to oxford cotton fabric (18x6cm) at 100% pick-up from solvent (e.g. THF and/or water). The fabric swatches were then dried, followed by an iron cure on  
10 high setting (cotton/linen) for the time specified.

After curing, the swatches were conditioned at 20°C, 65% relative humidity then the crease recovery angle (CRA) measured (using BS1553086). A sample of fabric (25mmx50mm)  
15 was folded in half forming a sharp crease and held under a weight of 1kg for 1 minute. On releasing the sample the crease opens up to a certain degree. After 1 minute relaxation, time the angle is measured. The fabric is tested in the warp direction only (hence maximum CRA is  
20 180°). Higher CRA therefore indicates less wrinkled fabric.

In examples 19-26 blocked isocyanates were pad applied to cotton fabric (18x6cm) at 100% pick-up from an appropriate solvent. The fabric swatches were then dried, followed by an  
25 iron cure on high setting (cotton/linen) for the time specified.

After curing, the swatches were conditioned at 20°C, 65% relative humidity then the crease recovery angle (CRA)  
30 measured (using a modified method based on BS1553086). A

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sample of fabric (25mmx50mm) is folded in half forming a sharp crease and held under a weight of 1kg for 1 minute. On releasing the sample the crease opens up to a certain degree. After 1 minute relaxation time the angle is measured. The fabric is tested in the warp direction only (hence maximum CRA is 180°). Higher CRAs correspond to less wrinkled fabrics.

**Example 14: Application of 2,4,6-Trichlorophenol Diester of Butanetetracarboxylic Acid**

---

CRA results obtained with a 5% solution of diester in THF (1g diester in 19g THF) are shown in Table 1 below.

Table 1

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	79	-	-	-
5% Diester	92	99	98	103

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples than with the untreated samples (UT). It can also be seen that the effect of a longer ironing-time on treated swatches is to further improve the results for the crease test (which occurs after the ironing step).

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**Example 15: Application of 2,4,5-Trichlorophenol Diester of Succinic Acid**

---

5 CRA results obtained with a 7.65% solution of diester in THF are given in Table 2 below:

Table 2

10

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	78	-	-	-
7.65% Diester	92	99	102	113

From these results it can again be seen that less creasing (higher CRA) was obtained with the treated samples than with the untreated samples (UT), and that a longer curing step  
15 further improved the results.

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**Example 16: Application of N-Hydroxysuccinimide Diester of Succinic Acid**

---

- 5 CRA results obtained with a 5.25% solution of diester in THF and water are given in Table 3 below:

Table 3

10

	CRA			
	10s iron	20s iron	30s iron	60s iron
UT Control	71			
5.25% Diester (THF)	87	88	93	95
5.25% Diester (water)	93	95	92	92

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples (both from THF and water) than with the untreated samples (UT). A water carrier gives good results with both a short and long a short curing/ironing step.

Example 17: Application of Vanillin Diester of Succinic Acid

CRA results obtained with 6.55% Diester in THF ( $19\text{cm}^3$ ) initially, increasing amount of water added are given in Table 4 below:

Table 4

	CRA - 60s Iron
UT Control	77
6.55% Diester in THF (no water added)	82
6.55% Diester in THF + $1\text{cm}^3$ H <sub>2</sub> O	86
6.55% Diester in THF + $2\text{cm}^3$ H <sub>2</sub> O	85
6.55% Diester in THF + $3\text{cm}^3$ H <sub>2</sub> O	88
6.55% Diester in THF + $5\text{cm}^3$ H <sub>2</sub> O	91

10

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples (both from THF and THF+water) than with the untreated samples (UT).

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**Example 18: Application of 4-Cyanophenol Diester of Succinic Acid**

---

5 CRA results obtained with a 5.45% solution of diester in THF are given in Table 5 below:

Table 5

10

	CRA - 60s Iron
UT Control	77
5.45% Diester	84

From these results it can be seen that less creasing (higher CRA) was obtained with the treated samples than with the  
15 untreated samples (UT).

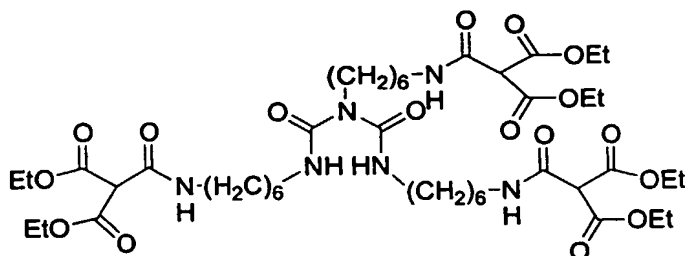


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**Example 19: Application of Hexylene diisocyanate biuret  
blocked with diethyl malonate**

---

5 The structure of this molecule is shown below.



10

Hexylene diisocyanate biuret blocked with diethyl malonate  
(trade name BI7963 ex. Baxenden Chemicals Ltd) was obtained  
as a 70% solution in 1-methoxy-2-propanol and diluted in THF  
15 to give a 2% solution. Results are given in table 6 below

**Table 6: CRA Results**

Ironing Time	CRA
UT control	76
Light iron (less than 2s)	90
2s	92
4s	93
6s	92
8s	95
10s	97

20

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In the case of the treated samples, it can be seen that even a very brief period of ironing gives a marked improvement in crease recovery. It is believed that this is due to the cross-reaction of the material with cellulose. It is also  
5 believed that this is an example of one of the isocyanate reactions which gives a true ester rather than a carbamate on reaction with cellulose.

10 **Example 20: Application of Hexamethylene diisocyanate  
blocked with Meldrum's Acid.**

---

Application was as described above from a 2% solution.

15 Results are given in table 6 below. It can be seen that crease recovery angles were improved as compared with the control.

**Table 6: CRA (2% solution in DCM)**

20

Ironing Time	CRA
UT Control	73
2s	83
6s	85
10s	84
20s	85

- 59 -

**Example 21: Application of Hexamethylene diisocyanate  
blocked with Phenol**

---

5 Application was as described above from a 2% solution.  
Results are given in table 7 below. It can be seen that  
crease recovery angles were improved as compared with the  
control.

10

**Table 7: CRA (2% solution in THF)**

Ironing Time	CRA
UT Control	73
2s	84
6s	94
10s	89
20s	89

**Example 22: Application of Hexamethylene diisocyanate  
blocked with Succinimide.**

---

15

Application was as described above from a 2% solution.  
Results are given in table 8 below. It can be seen that  
20 crease recovery angles were improved as compared with the  
control.

**Table 8: CRA (2% solution in DMAc)**

Ironing Time	CRA
UT Control	73
2s	94
6s	98
10s	99
20s	102

- 60 -

**Example 23: Application of Hexamethylene diisocyanate  
blocked with Sodium Bisulphite**

---

5 Application was as described above from a 1% solution.  
Results are given in table 9 below. It can be seen that  
crease recovery angles were improved as compared with the  
control.

10 **Table 9: CRA (1% solution in water)**

Ironing Time	CRA
UT Control	75
2s	78
6s	83
10s	85
20s	85

15 **Example 24: Application of Hexamethylene diisocyanate  
blocked with 4-Nitrophenol.**

---

Application was as described above from a 2% solution.  
Results are given in table 10 below. It can be seen that  
20 crease recovery angles were improved as compared with the  
control.

**Table 10: CRA (2% solution in DMAc)**

Ironing Time	CRA
UT Control	73
2s	77
6s	83
10s	95
20s	92

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**Example 25: Application of Hexamethylene diisocyanate  
blocked with 4-Methoxyphenol**

---

5

Application was as described above from a 2% solution.  
Results are given in table 11 below. It can be seen that,  
other than for very short ironing times, crease recovery  
angles were improved as compared with the control.

10

**Table 11: CRA (2% solution in DMAc)**

Ironing Time	CRA
UT Control	73
2s	73
6s	73
10s	84
20s	90

15

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**Example 26: Application of Hexamethylene diisocyanate  
blocked with Methyl salycilate**

---

5 Application was as described above from a 2% solution.  
Results are given in table 12 below. It can be seen that  
crease recovery angles were improved as compared with the  
control.

10

**Table 12: CRA (2% solution in THF)**

Ironing Time	CRA
UT Control	73
2s	87
6s	86
10s	87
20s	86

15 **Example 27: Application of Isoeuginol Diester of Succinic  
Acid.**

---

20 Upon application of the isoeuginol diester to cotton and  
subsequent ironing, a clove fragrance was released as the  
trans-esterification crosslinking occurred.

25